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<b>(21) International Application Number:</b> PCT/GB90/01808 <b>(22) International Filing Date:</b> 23 November 1990 (23.11.90)  <b>(30) Priority data:</b> 8926632.4                      24 November 1989 (24.11.89) GB  <b>(71) Applicant (for all designated States except US):</b> IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> CROOK, Pauline, Em- ma [GB/GB]; Julians, Bagby, North Yorkshire YO7 2PH (GB). FORREST, Iain, McPherson [GB/GB]; 30 Parkside, Lea, Preston, Lancashire PR2 1YS (GB).		<b>(74) Agents:</b> ROBERTS, Jonathan, Winstanley et al.; Imperial Chemical Industries plc, Group Legal Dept. Patents, P.O. Box 6, Bessemer Road, Welwyn Garden City, Hert- fordshire AL7 1HD (GB).  <b>(81) Designated States:</b> AT (European patent), AU, BE (Euro- pean patent), CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Euro- pean patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> POLYMER BLEND COMPOSITION			
<b>(57) Abstract</b>  Ternary blends of polyester, polyolefin and functionalised olefin polymer are strong tough materials showing little signs of incompatibility which can be fabricated into products by a variety of techniques including injection moulding, extrusion blow moulding, injection blow moulding and thermoforming (of extruded sheet).			

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Polymer Blend Composition

This invention relates to a polymer blend composition and in particular to a blend of a polyester and two types of olefinic polymer; a polyolefin and a functionalised olefinic polymeric material.

5 Aromatic polyesters, i.e. polyesters made from aromatic acids such as terephthalic acid, referred to herein simply as 'polyesters', are widely used materials. They are relatively impermeable to gasses and common organic solvents and can form strong tough moulded products. Despite their advantages, they do suffer from certain drawbacks which restrict  
10 their use. Injection moulded products made from polyesters often have regions, particularly at corners in the moulded product, that are much less tough than might be expected. This makes injection moulded polyester products liable to failure by brittle fracture especially at corners. In containers, such as paint containers, this is an obvious  
15 major disadvantage.

It is of course well known that polyethylene terephthalate is used in the manufacture of bottles by injection stretch blow moulding, in which a preform the plastic is made by injection moulding, put in a blowing mould and stretched and then blown to produce the moulded product. In  
20 making bottles from polyesters, the low melt viscosity of typical polyester resins means that the preform needs to be stretched to strengthen it prior to blowing. The effect of the initial axial stretching and the subsequent circumferential stretching in the blowing step is to bi-axially orient the polyester, thus markedly strengthening  
25 and toughening it so that the product is strong and tough and is not liable to brittle fracture in ordinary use, even in the storage of carbonated drinks.

It has been suggested to blend the polyester with polyolefins to overcome this lack of toughness in polyester products. Simple blends  
30 are not practical because the two different types of polymer are not compatible as is shown by the tendency of products made from such blends

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to fail mechanically by delamination. This incompatibility is described e.g. by Bataille, Boisse and Schreiber in Advances in Polymer Blends and Alloys Technology (Edited by M A Kohudic and Published by Technomatic Publishing Co. Lancaster and Basel) Volume 1 pp 12-16. These authors  
5 describe the two polymer (PP/PET) system, noting the general non-synergistic behaviour of simple blends ('Strong negative deviations are observed from the "rule of mixtures" behaviour...') on testing for e.g. permeability, and the "unspectacular results" i.e. showing no significant improvement, from the inclusion of a co-polymer of poly-  
10 propylene-acrylic acid as a possible coupling agent.

Further discussion of this incompatibility can be found in the earlier UK Patent Specification No. 1552637. This Specification seeks to overcome the incompatibility by blending polyesters, defined broadly and including polycarbonates, with a random copolymer made using a variety  
15 of monomers (selected from a list of eight types of monomers), and in which the random copolymer is dispersed in a matrix of the polyester as very fine particles having a particle size of from 0.001 to 1  $\mu$ m. Typical random copolymers exemplified are special ternary or quaternary (or higher) copolymers of monomers selected from the eight different  
20 types. This is not entirely satisfactory as the 'polyolefin' component is a highly specialised copolymer and has to be very finely dispersed.

We have adopted a different approach to this problem of incompatibility between polyesters and polyolefins by using an intimate three component blend of polyester and two types of olefinic polymer; one a polyolefin  
25 homo- or co-polymer and the other a graft modified olefin polymer, using similar amounts of each of the two types of olefinic polymer. This system shows little sign of incompatibility between the olefinic polymers and the polyester and can give strong, tough materials which can be processed (into products) by a wide range of techniques including  
30 injection moulding, injection blow moulding, extrusion blow moulding and thermoforming of extruded sheet. The use of similar amounts of the two types of olefinic polymer suggests that the functionalised olefinic polymer is not simply acting as a compatibilising agent for the polyolefin and the polyester. This is confirmed by microscopic

examination of the product which shows <sup>3</sup>identifiable dispersed particles of each of the two types of olefinic polymer.

Accordingly, the present invention provides a polymeric composition which is an intimate blend of from 70 to 98% by weight of at least one polyester and from 2 to 30% by weight of the combination of at least one  
5 polyolefin and at least one functionalised olefinic polymer wherein the weight ratio of polyolefin to functionalised olefinic polymer is from 1:3 to 3:1.

The polyester used in the invention is a polyester derived from an  
10 aromatic acid. In particular, the polyester will be a poly(alkylene)-phthalate polyester. Usually, acid residues will be derived from, at least predominantly, terephthalic acid although, as is described below, a proportion of isophthalic acid residues may be included in the polymer. The alkylene group will usually be ethylene, thus forming PET  
15 (as homopolymer or copolymer - see below), but other residues such as butylene groups can also be used. The main functional requirement for the polyester is that it can, as part of the composition of the invention, be fabricated into the desired end products. Thus, when the composition is to be used for articles having optimum impact strength  
20 properties, the requirements for the polyester are that it should be capable of being fabricated into a container, or the like, under conditions which provide the polyester in a form which is essentially amorphous. With a polyester such as a polyethylene terephthalate homopolymer this can be achieved in an injection moulding process using  
25 cold moulds, i.e. at a temperature of less than 30°C and preferably less than 10°C. Additionally, where a greater margin for maintaining the amorphous nature of the processed blend is desired, the use of a polyester having a higher molecular weight e.g. as measured by intrinsic viscosity (see below) can be beneficial. This is particularly useful  
30 where processing involves a hot forming stage (without melting) that might encourage crystallisation, as in the manufacture and use of thermoformable sheet. For even greater convenience the polyester can be one having a lower crystallisation rate than polyethylene terephthalate homopolymer. For example, inhibition of crystallisation of PET can be

provided by using additives which inhibit crystallisation or, more conveniently, by including comonomers, such as isophthalic acid as about 2% of the acid monomers, which disrupt chain packing and decrease crystallisation rates.

- 5 When the composition is used for injection moulding another requirement is that the polyester, which forms the matrix of the moulded article, should be readily melt processable. Generally, the intrinsic viscosity (IV) of the polyester, when it is a polymer or copolymer of ethylene terephthalate, (measured as described below) is from 0.3 to 1, particularly, between 0.4 and 0.8. Different end uses have different optimum values of IV. For injection moulding the IV of the PET is optimally from 0.5 to 0.75, particularly about 0.6; the use of lower IV material adversely affects the toughness of the product and the use of higher IV material can give process difficulties from the high melt viscosity of the polymer. For extrusion blow moulding, the IV is optimally at least about 0.7 and can be up to 1.0. For thermoformable extruded sheet, and products made from it such as trays, the IV is optimally at least about 0.5 and can be up to 1.0, which represents about the highest IV available for PET polymers commercially available; higher values could be used were they available.

- The polyolefin used in the composition of the invention is a crystalline polymer ethylene or propylene, especially crystalline forms of polyethylene (PE) such as high density polyethylene (HDPE) or linear low density polyethylene (LLDPE) or crystalline polypropylene (PP) such as isotactic polypropylene, or a copolymer of ethylene and propylene (EP), or a copolymer of ethylene and/or propylene with a minor proportion, that is up to 15% by weight, of another ethylenically unsaturated monomer. Desirably, the polyolefin has a melt flow index (MFI) of from 0.3 to 50 (measured as described below). The polyolefin may be polypropylene or a copolymer of propylene and ethylene containing, for example, between 5 and 15% by weight of ethylene. The use of such a copolymer can give products having higher impact strength than otherwise similar products made using a crystalline polypropylene homopolymer. Blends of more than one such polyolefin polymer may be used.

The functionalised olefinic polymer is a polymer of ethylene and/or propylene which has been graft polymerised with di-carboxylic acid or, and especially, anhydride, particularly maleic anhydride residues. Preferably, the graft residues are or include anhydride, especially maleic anhydride, residues which are retained at least partly unhydrolyzed in the resulting graft co-polymer. A functionalised olefin polymer including grafted maleic anhydride residues is referred to herein as being maleinised. The functionalised olefinic polymer appears to improve both the impact strength of the composition and compatibility between the polyester matrix and the polyolefin polymers in the composition. The (preformed) olefin polymer is typically one having rubbery characteristics, in particular a tensile modulus of less than 3,000 kg/cm<sup>2</sup> (ca. 294 MPa), such as an ethylene propylene rubber. The material grafted onto the olefinic polymer will typically be an ethylenically unsaturated monomer including the desired functional group. A particularly convenient way of carrying out such a grafting step is by extrusion compounding the rubber with the monomer under melt conditions in the presence of a free radical generating peroxide catalyst. The concentration of combined anhydride containing monomer will usually be from the range 0.05 to 5% and most desirably 0.1 to 2.0%, by weight of the olefin polymer.

For reasons that are not clear, we have found that it is desirable that the amount of polyolefin and functionalised olefin polymer should be approximately equal. Weight ratios close to one seem to be optimal but there is little fall off of properties in the ratio range 3:2 to 2:3, and significant gains are possible in the range 3:1 to 1:3. Outside this broad range the performance of the compositions is much less good.

The composition of the invention will usually be pre-blended prior to manufacture into end products. Unfilled blends made as described in more detail below are substantially colourless (white) translucent or pearlescent materials. Microscopic examination of these blends shows a matrix of the polyester with the polyolefin and functionalised olefin polymer as separate dispersed phases in the matrix. Typically, the dispersed phases are present as approximately spherical particles having

polyolefin phase enables the pigment to be supplied to the blend as a masterbatch in a suitable polyolefin such as polypropylene. This represents a particularly convenient way of pigmenting polyesters. Suitable pigments include titanium dioxide. Other non blend materials such as fillers, which can be reinforcing fibrous fillers such as glass, mineral, carbon or polymeric e.g. aramid, fibres, or non-fibrous fillers including inorganic fillers such as calcium carbonate or silica, can be included. The amounts of these materials used will usually be conventional. For pigments and fillers the total amount will typically be from 5 to 50 parts by weight per 100 parts by weight of the resin blend (phr).

However, where the end use of the composition of the invention requires maximum impact strength, it is highly desirable that the blend includes no materials of a type or a concentration which will cause the polyester to crystallise significantly under the moulding conditions used.

The composition of the invention is preferably used in the form of a pre-formed intimate blend of the components, prepared by melt blending. It is highly desirable that intensive mixing is applied during blending to ensure uniform distribution of the disperse phase polymers. This can suitably be done by using a twin screw extruder. The use of such an intensive mixing device is important as less intensive techniques may not give an adequately intimate blend. In particular, the use of a single screw extruder may not be satisfactory.

The compositions of the present invention can provide good barrier properties in the form of an intimate blend of the components of the composition. The compositions are suitable for providing barrier properties in the form of a single layer. This is clearly an advantage over the provision of barrier properties using multilayers, each of different composition, because apart from the ease of fabrication the eventual moulded or extruded products can be recovered as scrap without the need to separate differing materials. Despite the fact that the polymeric components of the blend are dissimilar materials the compositions of the invention provide articles which are much less prone



an average particle size (diameter) of from 2 to 4  $\mu\text{m}$ , usually 2.5 to 3  $\mu\text{m}$ . This morphology is different from that typically observed in compatibilised two polymer blends where the compatibilising agent is concentrated at the boundary between the two (otherwise incompatible) polymers. It is possible that some of the functionalised olefin polymer is located at the phase boundary between the polyolefin and the polyester (our examination has not enabled us to determine this), but even if this is so, the additional phase seems to contribute to the advantageous properties of the compositions of the invention in a way that we cannot explain. A particularly good blend can be made using PET, PP and graft maleinised ethylene/propylene copolymer and, thus, the invention includes in a particular and very desirable subsidiary aspect a polymeric composition which is an intimate blend of from 75 to 90% by weight of polyester and from 10 to 35% by weight of the combination of a polypropylene and a graft maleinised ethylene/propylene copolymer wherein the weight ratio of polypropylene to graft maleinised ethylene/propylene copolymer is from 3:2 to 2:3.

Where the blends of the invention is to be used in extrusion blow moulding, it is desirable that the amount of the functionalised olefin polymer is not excessive so as to avoid adverse effects on the processing characteristics of the final composition arising from uncontrolled changes in melt viscosity. In this end use, the amount of the functionalised olefin polymer will normally be kept to the minimum necessary to give the desired properties such as good impact strength.

The composition may contain various other additives, particularly antioxidants and/or stabilisers, pigments and fillers. The inclusion of pigments illustrates a further advantage of the invention. The present compositions have a high level of acceptability of typical pigment for plastics, without causing a deterioration in the impact strength of the blends. This desirable behaviour of the composition with respect to pigments is believed to arise because when the components are homogenised in the presence of the pigments, the pigments mostly end up dispersed in the polyolefin component (rather than the polyester component) of the blend. This effect of pigment concentration in the

to delamination than other compositions which have been proposed for single layer barrier containers, such as paint pots. The relative absence of evidence of delamination indicates that the blend is substantially compatible. This property of the blend provides compositions which have applications other than as single layer barrier materials.

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An important use for the compositions of the invention is in paint containers, particularly for paints employing an organic solvent. In addition to requiring barrier resistance to organic solvents, impact strength and ready mouldability this application requires a composition which can provide a good level of white opacity e.g. by including pigments such as titanium dioxide. Other end uses for the compositions of the invention include bottle tops, particularly as made by injection moulding, blow (injection or extrusion) moulded bottles and thermoformable sheet and products made from it by thermoforming the sheet. It is notable that blends of the invention can be used in extrusion blow moulding even for some grades of polyester that are by themselves not suitable for this fabrication method.

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A further advantage of the blends of the invention is that they are relatively cheap and can be used economically in disposable articles such as containers.

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The invention is illustrated by the following Examples. All parts and percentages are by weight unless otherwise indicated.

The following materials were used in the Examples:

5 Melinar B90S - polyethelene terephthalate IV = 0.6 from ICI  
Melinar B90N - polyethelene terephthalate IV = 0.78 from ICI  
Propathene HPE 110 - polypropylene copolymer MFI = 0.6 from ICI  
Exxcelor VA1801 - maleinised ethylene propylene copolymer from Exxon

#### Test and Measurement Methods

10 Intrinsic Viscosity (IV) - (of polyesters) was measured on a 1% solution in o-chlorophenol at 23°C.

Melt Flow Index (MFI) - (of polyolefins) was measured according to ISO 1133 at 230°C with a load of 2.16 kg (21.18 N).

Tensile strength to yield point (TS) - was measured by the method of ISO 527 on injection moulded tensile test samples.

15 Flexural modulus (FM) - was measured by the method of ISO 178 on injection moulded flexural test samples. Results are given in GPa.

20 Izod Impact Strength (Izod) - was measured by the method of ISO 180 on injection moulded test samples having a 0.25 mm (tip radius) milled notch. Tests were carried out on dry samples at ambient temperature (23°C) and on samples at -30°C. Results are given in kJ.m<sup>-2</sup>.

#### Preparation of blends

25 The polymer blends used in the Examples were made by drying the components of the blends in particle form to a moisture content of not more than 0.01%, dry blending the components and then mixing and extruding the blend using a Pfleiderer ZSK-30 twin screw extruder at a melt temperature of 295°C and a screw speed of 285 rpm (4.75 Hz). The extruded strands were water cooled, cut into pellets and dried.

1C  
Example 1

Various blends were injection moulded. Table 1 below shows the composition of the blends. Test specimens were injection moulded using a Demag Hamilton moulding apparatus at a barrel temperature maintained in the range 280 to 295°C. A chiller was used to keep the mould temperature within the range 10 to 15°C. Test data on injection moulded samples are set out in Table 2 below.

Example 2

Bottles were extrusion blow moulded using blends of the invention. Table 1 below sets out the compositions of the blends. Small bottles, 14 cm long and 275 ml capacity were extrusion blow moulded on a pilot extrusion blow moulding apparatus. The solvent barrier resistance of these bottles was tested by filling samples with different solvents, closing them by sticking aluminium foil over the mouth of each bottle using epoxy resin and assessing the weight loss on storage. The results of these tests are set out in Table 3 below. It will be noted that the PET grade (Melinar BS 90N) used in this Example is not suitable on its own for extrusion blow moulding.

Example 3

Blend compositions of the invention, as set out in Table 1 below, were extruded as 53 cm wide sheet using an Egon 1.25 inch (31.75 mm) sheet extrusion apparatus with a barrel temperature of 260°C. This sheet was then fed to a standard thermoforming machine to make food trays of 19x12x4 cm at a mould temperature of 23°C. The polyester in trays made in this way was amorphous. Increasing the temperature of the mould enabled the manufacture of trays in which the polyester was semi-crystalline.

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TABLE 1

Compositions of blends used in the Examples

	Example		Material	Amount
	No.			(%)
5	1	Sample 1	Melinar B90S	85
			Propathene HPE 110	7.5
			Exxcelor VA1801	7.5
		Sample 1	Melinar B90S	80
			Propathene HPE 110	10
10			Exxcelor VA1801	10
		Sample 1	Melinar B90S	70
			Propathene HPE 110	17.25
			Exxcelor VA1801	12.75
	2	Sample 1	Melinar B90N	85
15			Propathene HPE 110	7.5
			Exxcelor VA1801	7.5
		Sample 2	Melinar B90N	75
			Propathene HPE 110	12.5
			Exxcelor VA1801	12.5
20	3	Sample 1	Melinar B90S	85
			Propathene HPE 110	7.5
			Exxcelor VA1801	7.5
		Sample 2	Melinar B90S	80
			Propathene HPE 110	10
25			Exxcelor VA1801	10

<sup>12</sup>  
Table 2

Properties of injection moulded products made in Example 1

Sample No	FM (GPa)	TS (MPa)	Izod (kJ.m <sup>-2</sup> )	
			23°C	-30°C
1	1.54	37.6	10.72	7.01
2	1.37	34.0	32.00	9.58
3	1.03	26.2	(1)	8.15

(1) The sample was knocked out of the sample holder without being broken. This indicates that the sample is too tough to measure properly using this test.

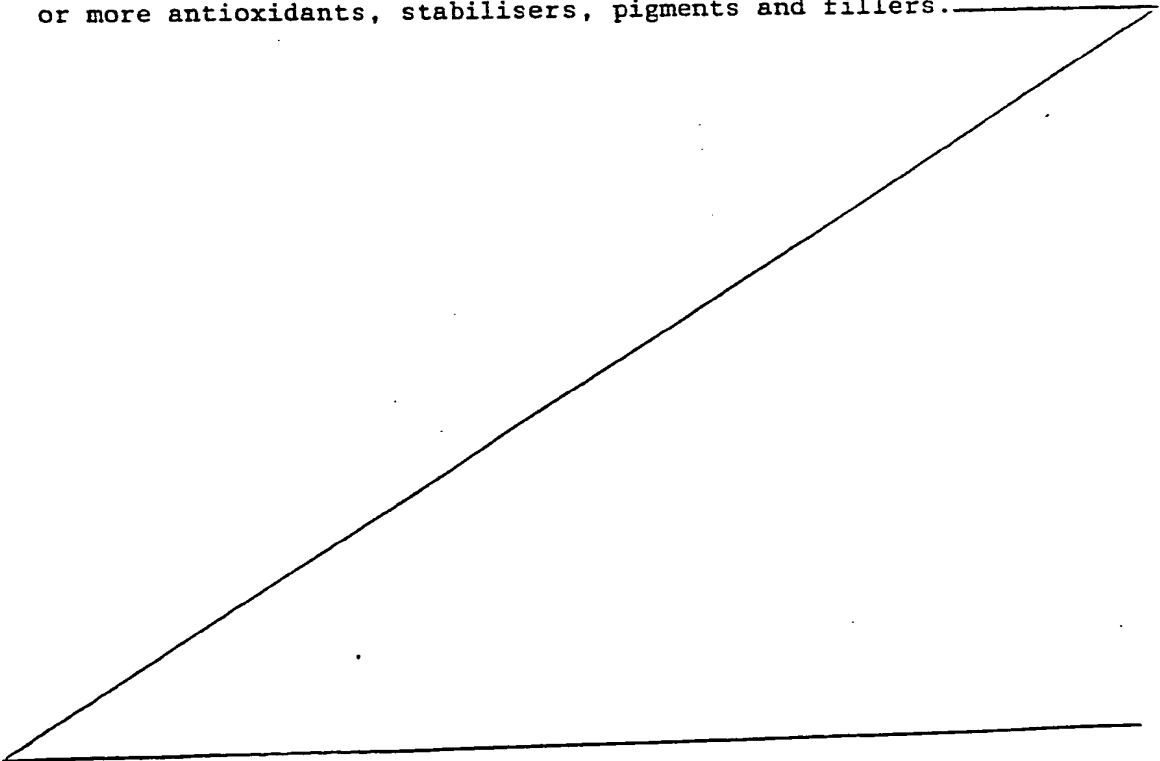
Table 3

Solvent barrier performance of bottles made in Example 2

Sample No.	Solvent	Amount in bottle (g)	Amount lost (g)
1	Xylene	259.64	0.00
	White Spirit	222.66	0.00
2	Xylene	258.02	0.00
	White Spirit	222.50	0.00

Claims

- 1 A polymeric composition which is an intimate blend of from 70 to 98% by weight of at least one polyester and from 2 to 30% by weight of the combination of at least one polyolefin and at least one functionalised olefinic polymer the weight ratio of polyolefin to functionalised olefinic polymer being from 1:3 to 3:1.
- 2 A polymeric composition as claimed in claim 1 wherein the polyester is a polyethylene terephthalate polyester having an intrinsic viscosity of from 0.3 to 1.
- 3 A polymeric composition as claimed in claim 2 wherein the polyethylene terephthalate includes about 2%, based on the total acid residues in the polyester, of residues of isophthalic acid.
- 4 A polymeric composition as claimed in claim 1 wherein the polyolefin is crystalline high density polyethylene, linear low density polyethylene or isotactic polypropylene.
- 5 A polymeric composition as claimed in claim 1 wherein the polyolefin has a melt flow index of from 0.3 to 50.
- 6 A polymeric composition as claimed in claim 1 wherein the polymer used to make the functionalised olefinic polymer is an ethylene propylene rubber having a tensile modulus of less than 3,000 kg/cm<sup>2</sup>.
- 7 A polymeric composition as claimed in claim 1 wherein the functionalised olefinic polymer is a polymer of ethylene and/or propylene which has been graft polymerised with di-carboxylic acid or anhydride.

- 8 A polymeric composition as claimed in claim 7 wherein the functionalised olefinic polymer has been graft polymerised with maleic anhydride and includes from 0.05 to 5% of maleic anhydride residues by weight of the olefin polymer.
- 9 A polymeric composition as claimed in claim 1 in which the polyolefin and functionalised olefin polymer are present as separate dispersed phases in a matrix of the polyester the dispersed phases being present as approximately spherical particles having an average particle size (diameter) of from 2 to 4  $\mu\text{m}$ .
- 10 A polymeric composition as claimed in claim 1 which is an intimate blend of from 75 to 90% by weight of a polyethylene terephthalate polyester and from 10 to 35% by weight of a combination of polypropylene and a graft maleinised ethylene/propylene copolymer the weight ratio of polypropylene to graft maleinised ethylene/propylene copolymer being from 3:2 to 2:3.
- 11 A polymeric composition as claimed in claim 1 which includes one or more antioxidants, stabilisers, pigments and fillers.
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# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01808

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 L 67/00, C 08 L 51/06, C 08 L 23/00														
<b>II. FIELDS SEARCHED</b> <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border: none;"> <tr> <td style="width: 20%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">C 08 L</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	IPC5	C 08 L								
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 70%;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 20%;">Relevant to Claim No.<sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0307802 (NIPPON PETROCHEMICALS COMPANY, LIMITED) 22 March 1989, see the whole document <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0337214 (SUMITOMO CHEMICAL COMPANY, LIMITED) 18 October 1989, see the whole document <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0177151 (SUMITOMO CHEMICAL COMPANY, LIMITED) 9 April 1986, see the whole document <div style="text-align: center;">--</div><div style="text-align: center;">-----</div></td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> </tbody> </table>			Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	EP, A2, 0307802 (NIPPON PETROCHEMICALS COMPANY, LIMITED) 22 March 1989, see the whole document <div style="text-align: center;">--</div>	1-11	A	EP, A2, 0337214 (SUMITOMO CHEMICAL COMPANY, LIMITED) 18 October 1989, see the whole document <div style="text-align: center;">--</div>	1-11	A	EP, A2, 0177151 (SUMITOMO CHEMICAL COMPANY, LIMITED) 9 April 1986, see the whole document <div style="text-align: center;">--</div> <div style="text-align: center;">-----</div>	1-11
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A	EP, A2, 0177151 (SUMITOMO CHEMICAL COMPANY, LIMITED) 9 April 1986, see the whole document <div style="text-align: center;">--</div> <div style="text-align: center;">-----</div>	1-11												
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<b>IV. CERTIFICATION</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">           Date of the Actual Completion of the International Search  <div style="border: 1px solid black; padding: 5px; text-align: center;">28th February 1991</div> </td> <td style="width: 50%; border: none;">           Date of Mailing of this International Search Report  <div style="border: 1px solid black; padding: 5px; text-align: center;">22 MAR 1991</div> </td> </tr> <tr> <td style="width: 50%; border: none;">           International Searching Authority  <div style="border: 1px solid black; padding: 5px; text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; border: none;">           Signature of Authorized Officer  <div style="border: 1px solid black; padding: 5px;">             Mme N. KUIPER  </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="border: 1px solid black; padding: 5px; text-align: center;">28th February 1991</div>	Date of Mailing of this International Search Report <div style="border: 1px solid black; padding: 5px; text-align: center;">22 MAR 1991</div>	International Searching Authority <div style="border: 1px solid black; padding: 5px; text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="border: 1px solid black; padding: 5px;">             Mme N. KUIPER  </div>								
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SA 42119

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The members are as contained in the European Patent Office EDP file on 31/01/91  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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